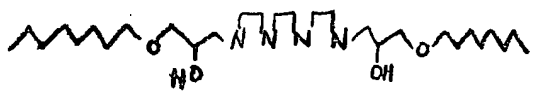
Contains 1,2,3 equivalent adducts of DETA + MW 202

"hit" → 

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(54) Method to Produce the Compound Which Has Sterilizing Ability

(21) Application No. : S44-105442

(22) Application Date : December 30, 1969

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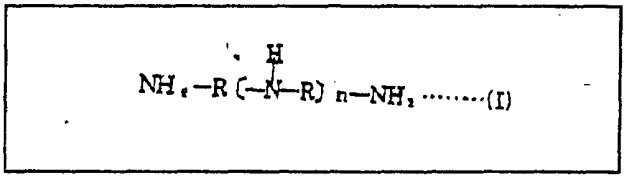
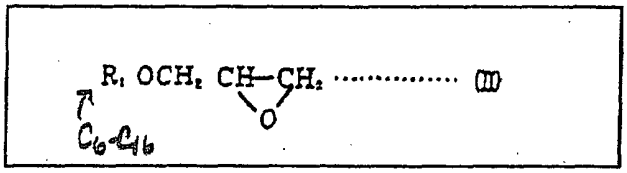
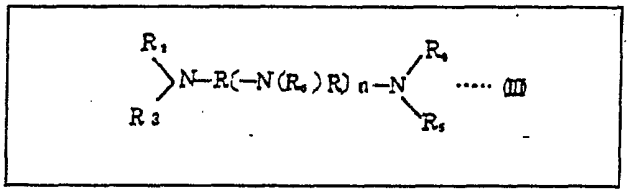
Detailed Explanation of the Invention

This invention relates to the method to produce the compound which has excellent sterilizing ability, and in particular, it relates to the method to produce the compound

which has sterilizing ability that is characterized by the fact that the glycidyl ether derivative that can be indicated by the general formula (II) is reacted with the poly alkylene poly amine that can be indicated by the general formula (I), and which is comprised of the compound that can be indicated by the general formula (III).







Here, in the above mentioned general formulas, R indicates an alkylene group with 2 to 3 carbon atoms. R_1 indicates a lipophilic group comprised of an alkyl group or an alkyl allyl group that has 6 to 16 carbon atoms. R_2 indicates a lipophilic group that can be indicated by the formula, R_1 - OCH_2 CH (OH) - CH_2 .}. R_3, R_4, R_5 and R_6 can be the same or different hydrogen atoms or lipophilic groups that are the same as R?? (*illegible*). n can be 1 or 2.

The poly alkylene poly amines that can be indicated by formula (I) are for example, di-ethylene tri amine, tri ethylene tetramine, di- propylene tri amine, tri propylene tetramine, and di- tri methylene tri amine, etc. The glycidyl ether derivatives that can be indicated by formula (II) are for example, octyl glycidyl ether, lauryl glycidyl ether, iso tri

decyl glycidyl ether, and nonyl phenyl glycidyl ether, etc. Depending on the compounds in the above mentioned formulas (I) and (II), the compound with formula (III) can be obtained.

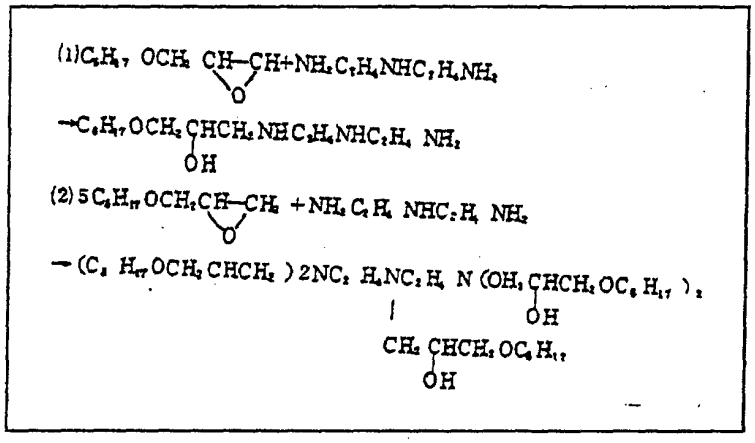
Until now, in the non- medical fields, organic mercury compounds and organic tin compounds, etc., have been used normally as the sterilizing agents and (mold? *illegible*) prevention agents because of their excellent effects. However, these organo metallic compounds have great disadvantages such as that their residual toxicity is large, so that the non- metal compounds are preferred for this use, but the effect of non-metal compounds is insufficient, so that the organo metallic compounds are presently used out of necessity.

The inventors of this invention discovered that the compounds that can be indicated by the above mentioned general formulas have excellent sterilizing ability and also that they have a (mold? *illegible*) prevention effect that is as good as that of the organic tin compounds, and this invention was completed.

The compound that can be indicated by the above mentioned general formula (III) can be obtained by reacting the poly alkylene poly amine that can be indicated by the above mentioned general formula (I) with the glycidyl ether derivative that can be indicated by the general formula (II) and which can be obtained by the normal reaction of a high rank alcohol and epi chloro hydrine.

This glycidyl ether derivative easily causes an addition reaction with a primary amine or a secondary amine, and produces a secondary amine or a tertiary amine, respectively.

The reaction equations in this invention are as follows.



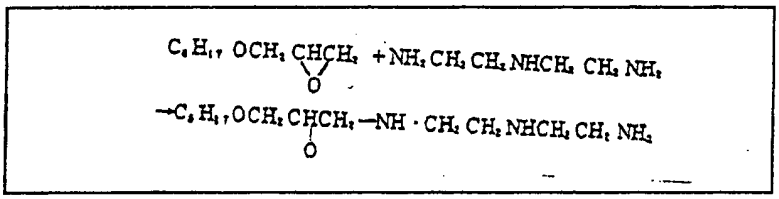
If necessary, the reaction product of this invention can be purified by distillation under reduced pressure, etc., and further, these reaction products can be reacted with an inorganic acid or an organic acid to make the inorganic acid salt or the organic acid salt.

Next, actual examples of this invention will be shown.

Example 1

29 parts (weight parts - this is the same for the following also) of di- ethylene tri amine was heated to 160 °C, and 70 (*it is not clear what implies here, but that is what the original says, Translator*) of 2 ethyl hexyl glycidyl ether was dropped in, and it was reacted at 180 °C, and thus, the reaction product, of which the main material was mono (3- octa oxy -2- hydroxy propyl) di- ethylene tri amine, was obtained. (This product is

called MOA -3.) The amine value of this material was 537, and the oxirane acid? (*although the text says acid, this may be a typo of oxygen, Translator*) % was 0. The reaction equation is as follows.



The amine value is the value which indicates the number of mg of potassium hydroxide that is equivalent to the amount of acid required to neutralize the total amines included in 1 g of sample. In order to measure this, 100 to 200 mg of sample was accurately weighed, and this was put in a 100 mL beaker, and 50 mL of glacial acetic acid was added, and it was titrated with 0.1 N- per chloric acid (potentiometric titration).

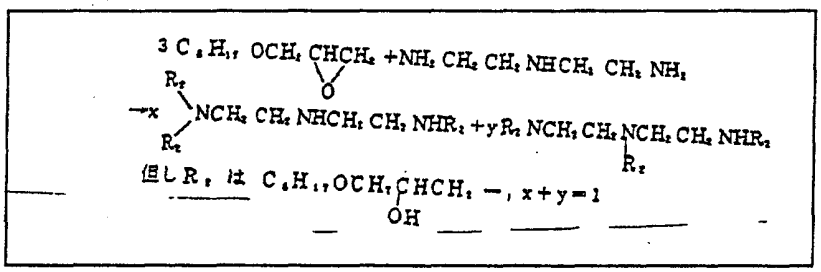
Oxirane oxygen % indicates the weight % of oxirane oxygen in the sample which was calculated from the amount of halogenated hydrogen that was added to the sample.

In order to measure this, 0.5 g of sample was accurately weighed, and it was put into a flat bottom flask with three openings with a stopper, and 25 mL of 0.2 N- hydrochloric acid dioxane solution was added, and the sample was dissolved, and thereafter, it was left for 15 minutes at normal temperature. Next, 25 mL of neutral ethanol and about 5 drops of phenolphthalein indicator were added, and the remaining hydrochloric acid was titrated with a 0.1 N- methanol potassium standard solution.

Example 2

31 parts of di- ethylene tri amine and 168 parts of 2- ethyl hexyl glycidyl ether were reacted the same as in Example 1, and the reaction product, of which the main material was tri (3- octa oxy -2- hydroxy propyl) di- ethylene tri amine, was obtained. (This product is called TOA -3.) The amine value of this material was 223, and the oxirane oxygen % was 0. The reaction equation is as follows.

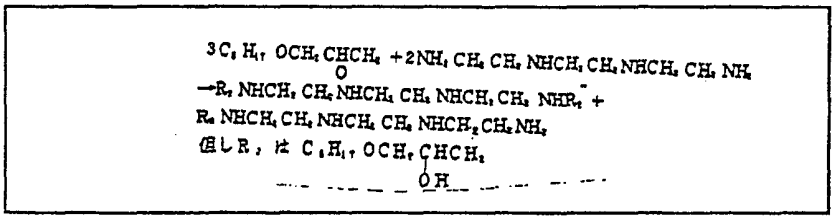
3 equivalent adduct



Here, R_2 is $C?H_{17}$ OCH_7 C (OH) HCH_2 -, and x + y = 1.

Example 3

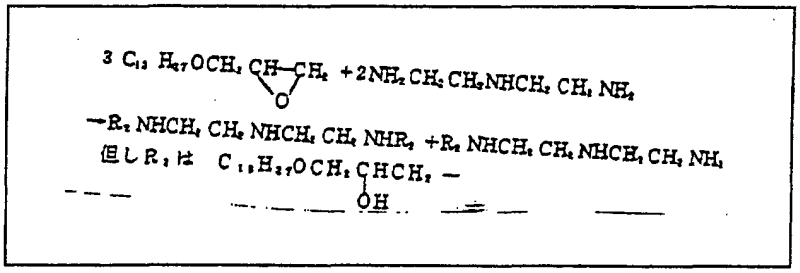
26 parts of tri ethylene tetramine and 50 parts of n- octyl glycidyl ether were reacted the same as in Example 1, and the reaction product, of which the main material was di (3- octa oxy -2- hydroxy propyl) tri- ethylene tetramine, was obtained. (This product is called MDOA -4.) The amine value of this material was 466, and the oxirane oxygen % was 0. The reaction equation is as follows.



Here, $R_?$ is $C?H_{17}$ $OCH_?$ C (OH) HCH_2 .

Example 4

19 parts of di ethylene tri amine and 70 parts of iso- tri decyl glycidyl ether were reacted the same as in Example 1, and the reaction product, of which the main materials were mono and di (3- tri decyl oxy -2- hydroxy propyl) di- ethylene tri amine, was obtained. (This product is called MDTA -3.) The amine value of this material was 300, and the oxirane oxygen % was 0. The reaction equation is as follows.



Here, R_2 is $C_{19?}$ $H_{27?}$ OCH_2 C (OH) HCH_2 -.

Example 5

103 parts of di ethylene tri amine and 276 parts of nonyl phenyl glycidyl ether were reacted the same as in Example 1, and the reaction product, of which the main materials was mono (3- nonyl phenoxy -2- hydroxy propyl) di- ethylene tri amine, was obtained. (This product is called MNPA -3.) The amine value of this material was 429.

Example 6

145 parts of methyl imino propyl amine and 186 parts of 2- ethyl hexyl glycidyl ether were reacted the same as in Example 1, and the reaction product, of which the main materials were N_1 - mono (3- octa oxy -2- hydroxy propyl) N_2 , methyl di- propylene tri amine, was obtained. (This product is called MOA -3M.) The amine value of this material was 496.

The test results for each product of the above mentioned Examples 1 to 6 are shown next.

Test 1

Phenol coefficient for various bacteria.

The test method followed the "Hygiene test guide" edited by the Ministry of Health and Welfare.

Table 1. Phenol Coefficient for Various Bacteria.

	Typhoid bacillus	Micrococcus pyogenes	Dysentery bacillus
10 % solution of MOA -3 hydrochloric acid salt	90? *illegible*	43	110
10 % solution of MOA -3 acetic acid salt	83?	43	100
10 % solution of TOA -3 hydrochloric acid salt	89?	40	110
10 % solution of MDOA -4 hydrochloric acid salt	56	20	67
10 % solution of MDTA -3 hydrochloric acid salt	55	23	78
10 % solution of MNPA -3 hydrochloric acid salt	78	23	36
10 % solution of MOA -3M hydrochloric acid salt	40	44	44

Reference Example

When 20 parts of ethylene diamine and 62 parts of octyl (2- ethyl hexyl, the same in the following) glycidyl ether were reacted the same as in Example 1, the reaction product, of which the main material was mono (3- octa oxy -2- hydroxy propyl) ethylene di- amine, was obtained. (This product is abbreviated as MOA -2.) Under the same type of conditions, the reaction of 47 parts of tetra ethylene pentamine and 47 parts of octyl glycidyl ether gave the reaction product of which the main material was mono (3- octa oxy -2- hydroxy propyl) tetra ethylene pentamine. (This product is abbreviated as MOA -5.) Also, the reaction of 13 parts of ethylene diamine and 62 parts of octyl glycidyl ether gave the reaction product of which the main material was mono and di- (3- octa oxy -2- hydroxy propyl) ethylene diamine. (This product is abbreviated as MDOA -2.), and the reaction of 32 parts of tetra ethylene pentamine and 47 parts of octyl glycidyl ether gave the reaction product of which the main material was mono and di- (3- octa oxy -2- hydroxy propyl) tetra ethylene pentamine. (This product is abbreviated as MDOA-5.)

The phenol coefficient with typhoid bacillus was tested for each reaction product in the above mentioned Reference Examples, and the results are shown in the following Table 1'.

Table 1'

Chemical	Phenol coefficient to typhoid bacillus
10 % solution of MOA -2 hydrochloric acid salt	20
10 % solution of MOA -5 hydrochloric acid salt	17
10 % solution of MDOA -2 hydrochloric acid salt	22
10 % solution of MDOA -5 hydrochloric acid salt	17

Test 2

The growth- prevention- concentration for three types of bacteria (temporarily, these are called stubs A, B and C) that were separated from decayed machine work oil, was obtained by the sequential dilution method (double dilution method).

Culture medium used : Normal bouillon culture medium

Culturing : 48 hours at 37 °C

Table 2. Growth Preventive Concentration for Each Chemical

Chemical agent	Bacteria tested		
	Stub A	Stub B	Stub C
MOA -3	PPM 5	PPM 5	PPM 5
TOA - 3	5	5	5
Phenyl mercury di naphthyl methane di- sulfonate 10 %	50	50	100
Mixture of di- brom salicyl anilide and tri brom salicyl anilide	100	50	200
Penta chloro phenol	100	50	250

Note : Less than 5 ppm, was not tested.

Test 3

The same test as Test 2 was performed for the mold (white mold) separated from the same decayed machine work oil used in Test 2.

Culture medium used : Saburo bouillon culture medium

Culturing : 1 week at 25 °C

Table 3. Growth Preventive Concentration to the Mold

Chemical agent	Growth preventive concentration

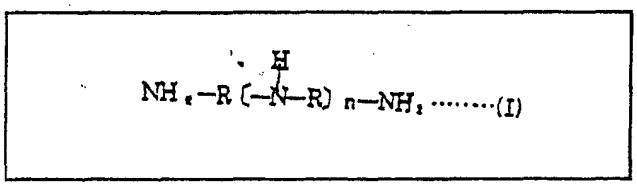
MOA -3	PPM 10
TOA - 3	10
Phenyl mercury di naphthyl methane di- sulfonate 10 %	5
Mixture of di- bromo salicyl anilide and tri bromo salicyl anilide	10
Penta chloro phenol	20

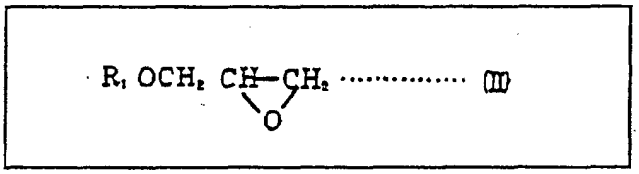
From the results of each test mentioned above, it is extremely clear that the germicidal agent that can be obtained by this invention has an excellent effect.

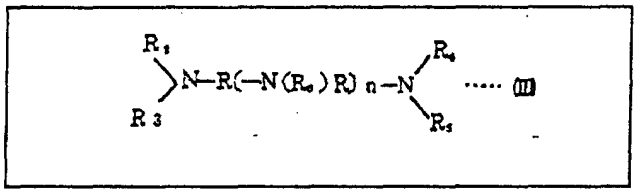
(57) Scope of the Patent Application

Claim 1.

Method to produce the compound that has sterilizing ability which is characterized by the fact that the glycidyl ether derivative that can be indicated by the general formula (II) is reacted with a poly alkylene poly amine that can be indicated by the general formula (I), and which is comprised of the compound that can be indicated by the general formula (III).







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(56) Reference:

Chemical Abstracts Vo.. 53, 17953d (1959)